



Short communication

Synthesis and characterization of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ intermediate-temperature electrolyte using conventional solid state reactionMinxia Li^a, Yaohui Zhang^{a,b,*}, Maozhong An^b, Zhe Lü^a, Xiqiang Huang^a, Juncheng Xiao^a, Bo Wei^a, Xingbao Zhu^a, Wenhui Su^a^a Center for Condensed Matter Science and Technology, Department of Physics, Harbin Institute of Technology, Harbin 150001, PR China^b School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, PR China

HIGHLIGHTS

- Pure phase LSGM powder is prepared by solid state reaction at 1,400 °C.
- The prepared LSGM provides an excellent ionic conductivity of 0.08 S cm⁻¹ at 800 °C.
- The LSGM powder has a fine particle size and narrower particle size distribute.
- The LSGM powder is suitable to fabricate dense electrolyte membranes (20–25 μm).

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ABSTRACT

The perovskite-type $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM9182) with high oxygen-ionic conductivity is successfully synthesized using conventional solid-state reaction. The phase composition, grain size distribution, relative density, and oxygen-ionic conductivity of the samples are studied. The XRD result shows that the main perovskite LaGaO_3 phase can be produced at 1,250 °C, with trace amount of second phase LaSrGaO_4 . When the temperature increases to 1,400 °C, the pure phase LSGM can be obtained. The relative density of LSGM pellets sintered at 1,400 °C reaches 98.08%. The average grain size of final powders is ~0.12 μm, which is appropriate for the deposition of LSGM electrolyte film. The ideal oxygen-ionic conductivities of 0.04, 0.06, and 0.08 S cm⁻¹ can be obtained at 700 °C, 750 °C, and 800 °C, respectively. Porous anode supported single cells with LSGM electrolyte film are fabricated using the as-prepared LSGM powders and the cells provide an open-circuit voltage of above 1.0 V, revealing that the LSGM film is gas-tight and crack-free.

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1. Introduction

Solid oxide fuel cell (SOFC) is a promising energy conversion device, which has attracted considerable attention due to its all-solid-state structure, high efficiency, low cost, high level of waste-heat utilization, and greater fuel flexibility [1–3]. Yttria-stabilized zirconia (YSZ) is the most widely used electrolyte materials so far [4,5]. However, SOFCs with YSZ electrolyte must be operated at high temperature up to 800 °C–1,000 °C owing to the fast decrease of oxygen-ion conductivity of YSZ with decreasing of the

temperature. High temperature operation brings serious troubles, i.e., electrode and sealing materials selection, chemical compatibility between electrodes and electrolytes [6,7]. Development of new electrolyte materials with high ionic conductivity at intermediate temperature (600 °C–800 °C) is a feasible approach to overcome the above-mentioned drawbacks of high temperature operation [8–10]. Doped-Bi₂O₃ and doped-CeO₂ electrolytes satisfy the demand of conductivity, but the structure instability restricts their applications in SOFCs [11–15]. Strontium and magnesium-doped lanthanum gallate (LSGM) exhibits good performance at intermediate temperature, such as excellent oxygen-ionic conductivity (several times higher than that of YSZ), negligible electron conductivity, high mechanical strength, and good chemical stability over a wide oxygen partial pressure range [16–18]. However, pure phase LSGM is difficult to synthesize, and the co-existing impurity phases, LaSrGaO_4 and $\text{LaSrGa}_3\text{O}_7$ could reduce the conductivity severely. Unfortunately, the synthesis of pure

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phase LSGM electrolyte powder with high oxygen-ionic conductivity is still a critical issue for development of intermediate-temperature SOFCs based on LSGM electrolyte.

Generally, sol–gel, glycine-nitrate combustion and solid state reaction were selected frequently to prepare the electrolyte and electrode powders. For sol–gel and glycine-nitrate combustion, the starting materials can be mixed homogeneously at molecular or atomic levels in solution, and fine powders with few secondary phase can be obtained [19–21]. Huang *et al.* synthesized $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ powder using sol–gel with ammonium hydroxide as complexing agent and they obtained pure perovskite phase at 1,350 °C [19]. The glycine-nitrate combustion was selected to prepare $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$ by Cong *et al.* Their results showed that the impurity phase of $\text{SrLaGa}_3\text{O}_7$ existed in the samples after sintered at 1,400 °C. When the temperature further increased to 1,550 °C, the impurity phase disappeared and powders with pure phase could be obtained [20]. Chae *et al.* discussed the effect of cobalt doping to the property of Sr and Mg-doped LaGaO_3 . They synthesized $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ by means of carbonate co-precipitation using ammonium carbonate as precipitant, the pure phase of LSGM was produced by calcination the precursor at 1,400 °C for 6 h [22]. Chen *et al.* reported a new method called low temperature hydrothermal urea precipitation process to synthesize $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$. In their paper, the synthesis temperature was controlled at 900 °C and an oxygen-ionic conductivity of 0.056 S cm^{-1} was obtained at 800 °C [23]. The liquid synthesis approaches have shown an advantage of easy to get nano-sized powder with single phase at lower temperature. Apparently, this method needs the procedures of dissolution, mechanical agitation, dewatering, drying, and repetitive sintering process, leading to a complex process. In some cases the liquid method needs expensive metal alkoxide precursors, which make the cost control become another challenge [24].

In this paper, simple and cost-effective solid state reaction was selected to prepare pure LSGM powder. The phase composition, particle size, grain size distribution and oxygen-ionic conductivity of the prepared samples were studied. The LSGM electrolyte films supported by porous substrate were also prepared using the as-synthesized LSGM powders.

2. Experimental

2.1. Powder preparation

La_2O_3 (99.99%), SrCO_3 (99%), Ga_2O_3 (99.99%), MgO (98%) were used as starting materials. La_2O_3 and MgO were pre-calcined at 1,000 °C for 2 h. Stoichiometric amount of La_2O_3 , SrCO_3 , Ga_2O_3 , and MgO were mixed thoroughly in an agate mortar, and then the mixed powder was ball-milled for 24 h using ethanol as media. The mixture was dried and pressed into pellets, and then sintered at 1,250 °C for 20 h. In order to accelerate the solid state reaction, the ball-milling, pressing, and sintering were repeated. The final powders were sintered at 1,400 °C for 4 h to get pure phase LSGM9182.

2.2. LSGM films deposition and sintering

In order to evaluate the feasibility of electrolyte film fabrication using prepared powders as starting materials, LSGM powders and binder (terpinol and ethylcellulose) were mixed together, and grinded sufficiently to get LSGM slurry. Then, the slurry was deposited on porous anode substrate by spin-coating technique. After dried at 400 °C, the pellets were finally sintered at 1,400 °C for 4 h to densify the LSGM films.

2.3. Characterization

The phase analysis of synthesized powders was studied using X-ray Diffractometer (UK, Bede Scientific Ltd., Cu K α radiation, operated at 40 kV, 45 mA; $\lambda = 0.15418 \text{ nm}$), the XRD diffraction was collected in 20°–90° angle range and the step width is 0.02°.

The grain size distribution of powder was measured using Malvern Mastersizer 2000 laser particle size analyzer. The powder was added to deionized water and dispersed by ultrasonic before test. Sodium Hexametaphosphate (NaPO_3)₆ was used as dispersant during the measurement.

The conductivities of sintered pellets were calculated from a.c. impedance spectra data that were measured using BiStat potentiostat (Bio-logic SAS, VSP s/n: 0315) with the software Ec-Lab. The sintered pellets (13 mm in diameter, 0.5–0.8 mm in thickness) were coated with silver paste as symmetrical electrodes, and the area of each electrode is 0.26 cm^2 . The measuring temperature was 550 °C–800 °C, the frequency ranged from 0.1 Hz to 10^6 Hz . The measurements were carried out in air at an a.c. voltage amplitude of 50 mV. The original impedance data was analyzed by Z-view 2.0 software.

The microstructure of the porous anode supported LSGM films was tested using scanning electron microscope (SEM, Hitachi S-570, Japan).

3. Results and discussion

3.1. Phase analysis of XRD

The XRD of powders prepared by solid-state reaction was shown in Fig. 1. It is obvious that the main phase of LaGaO_3 was formed at a lower temperature of 1,250 °C, however, accompanied with trace amount of LaSrGaO_4 . It is necessary to increase the sintering temperature to complete the solid state reaction. From the Fig. 1 (a), it can be seen that the sample sintered at 1,400 °C only contains the pure LSGM phase, while the peak of Ag comes from the Ag current collector in electrode. The present results indicate that LSGM powder with trace amount of LaSrGaO_4 can be prepared successfully at a lower temperature of 1,250 °C by the conventional solid-state reaction without any additive.

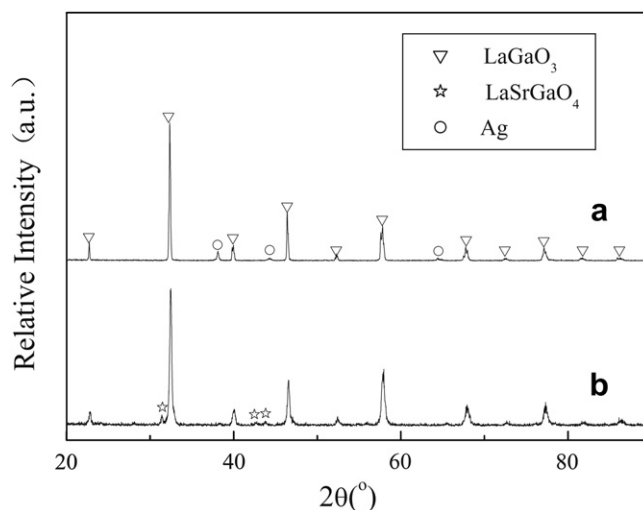


Fig. 1. XRD of the synthesized powders and the samples sintered at different temperatures: (a) 1,400 °C; (b) 1,250 °C.

3.2. Grain size distribution of LSGM powders

Application of thin film electrolyte is an effective approach to lower the operating temperature of SOFCs. Grain size of LSGM powders plays an important role for the deposition of electrolyte film. The particle size of powders influences the density of the film and thus determines the open-circuit voltage and ohmic resistance of the full cell. For comparison, the particle size of prepared LSGM powder sintered at 1,250 °C and TOSOH YSZ used frequently was plotted together in Fig. 2. It can be seen that the both powders exhibit bimodal distribution model, the left peak corresponds to the primary particles in the powders and the right one is the reflection of aggregates, i.e., the second particles. The commercial TOSOH YSZ powder has an average size of about 0.42 μm and 90 vol. % of the aggregate is less than 1.0 μm . For the as-prepared LSGM powder, the average size is 0.12 μm and 100 vol. % of the agglomerate is less than 1.0 μm . It can be readily seen that the LSGM powder has a smaller particle size and narrower particle size distribution than those of the commercial TOSOH YSZ powder.

According to the prior reports, compared with the liquid synthesis process such as sol–gel and glycine-nitrate combustion, the difficulties of solid-state reaction include that it is difficult to get pure phase LSGM powders with fine particle size and narrow particle size distribution. Here, pure phase LSGM powders with fine size were prepared by means of the conventional solid state reaction. The fine powders make it easy to get dense thin LSGM electrolyte films on porous substrates without peel-off and crack (see below).

Fig. 3 shows a cross-sectional image of porous anode supported LSGM film after sintering at 1,400 °C for 4 h. The LSGM layer is 20 μm thick, and relatively dense with ignorable closed pores. Based on this electrolyte film, several single cells were fabricated and tested between 550 °C and 650 °C using dry hydrogen as fuel and air as oxidant. In the measuring temperature range, the cells provide an open-circuit voltage of higher than 1.0 V, indicating that the LSGM film is gas-tight and suitable to be used as electrolyte for intermediate temperature SOFCs (IT-SOFCs).

3.3. Conductivity

The a.c. impedance spectra were measured using the samples of LSGM pellets sintered at 1,400 °C for 4 h, with a relative density of 98%. It can be seen from Fig. 4 that the depressed semi-circles on the intermediate- and low-frequency correspond to the electrode polarization resistance while the high-frequency intercept on the

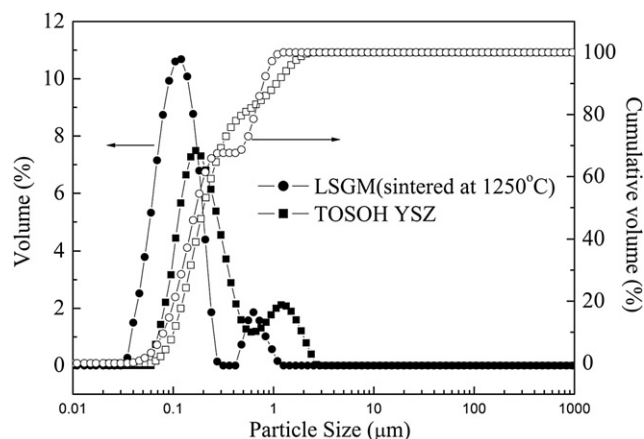


Fig. 2. Particle size distribution of LSGM powders (sintered at 1,250 °C) and commercial YSZ powders.

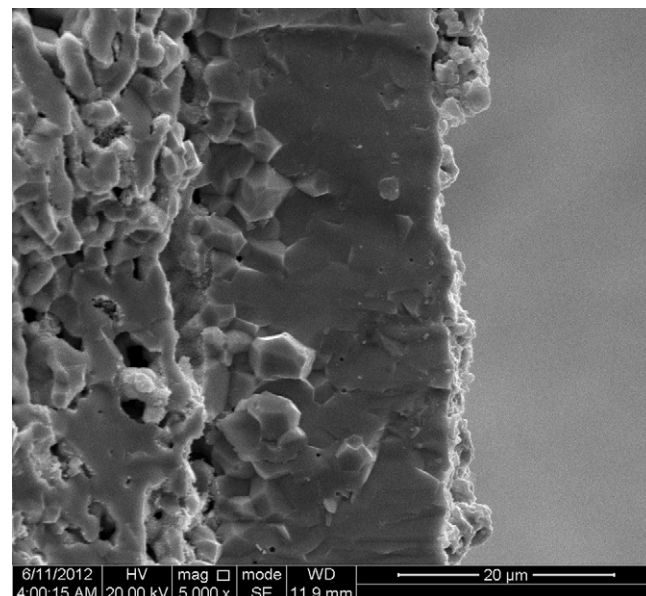


Fig. 3. Cross-sectional image of LSGM film of a single cell.

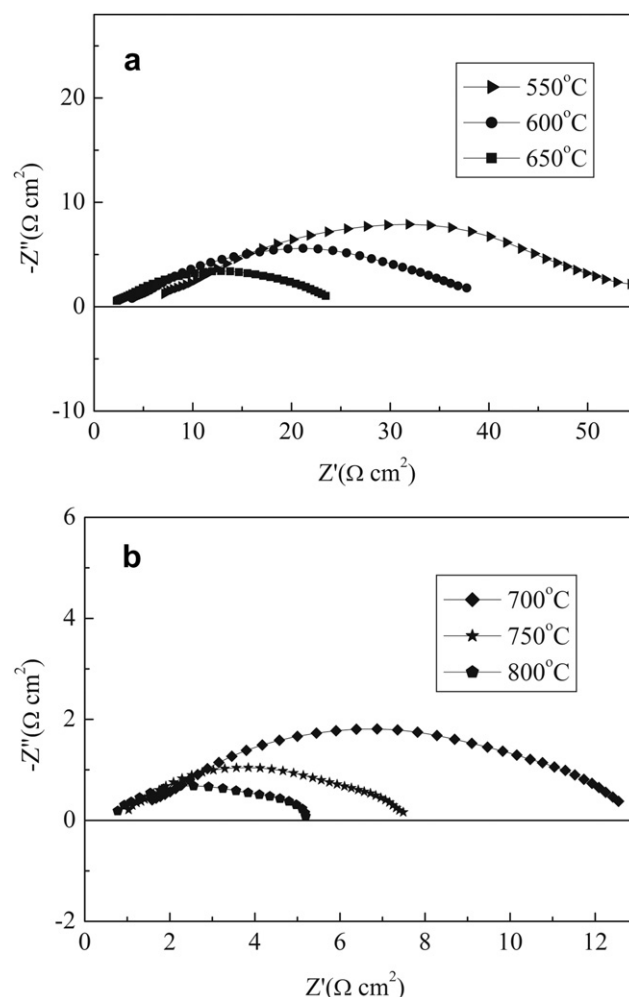


Fig. 4. Impedance spectra for the LSGM sample sintered at 1,400 °C for 4 h.

Table 1
Conductivity of synthesized LSGM9182 at 550 °C–800 °C.

| Temperature (°C) | Ohmic resistance <i>R</i> (Ω) | Ionic conductivity σ (S cm ⁻¹) |
|------------------|-------------------------------|---|
| 550 | 27.34 | 0.0079 |
| 600 | 14.31 | 0.0150 |
| 650 | 8.44 | 0.0254 |
| 700 | 5.20 | 0.0413 |
| 750 | 3.58 | 0.0600 |
| 800 | 2.67 | 0.0804 |

Table 2
Conductivity of LSGM samples prepared by different methods.

| Synthesized method | Composition of electrolyte | Conductivity at 800 °C (S cm ⁻¹) | Data source |
|---|--|--|-------------|
| Solid-state | La _{0.9} Sr _{0.1} Ga _{0.8} Mg _{0.2} O _{3-δ} | 0.08 | This paper |
| Glycine–nitrate | La _{0.8} Sr _{0.2} Ga _{0.85} Mg _{0.15} O _{3-δ} | 0.06 | Ref. [20] |
| Carbonate coprecipitation | La _{0.9} Sr _{0.1} Ga _{0.8} Mg _{0.2} O _{2.85} | 0.045 | Ref. [22] |
| Sol-gel method | La _{0.9} Sr _{0.1} Ga _{0.8} Mg _{0.2} O _{2.85} | 0.11 | Ref. [19] |
| Hydrothermal urea precipitation process | La _{0.8} Sr _{0.2} Ga _{0.8} Mg _{0.2} O _{2.8} | 0.056 | Ref. [23] |

real axes reflects the ohmic resistance of the LSGM electrolyte. Based on the impedance data and the geometric dimension of the LSGM pellets, the conductivity can be calculated according to the formula of $\sigma = L/RS$. Where, σ is the ionic conductivity, L the thickness of the sample, R the ohmic resistance, and S the area of the Ag electrode.

The conductivity data were listed in Table 1. It can be seen that the conductivity ~ 0.025 S cm⁻¹ at 650 °C was obtained, which is close to that of YSZ at 800 °C. The conductivity of LSGM reaches 0.08 S cm⁻¹ at 800 °C. In recent years, many researchers have synthesized LSGM using different approaches, and tested the performances of the products, especially the ionic conductivity. Table 2 shows the conductivity of LSGM with different composition synthesized by different methods. In theory, the conductivity of La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-δ} and La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8} is expected to be higher than that of La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-δ}, because of the higher doping level of Sr and Mg. However, the data listed in Table 2 show some difference, which is probably caused by synthesized process. The LSGM9182 synthesized in the present work shows a good conductivity compared with the prior data.

4. Conclusions

The intermediate-temperature electrolyte LSGM with perovskite structure was synthesized using conventional solid-state reaction. The XRD pattern shows that the synthesis temperature

can be controlled as low as 1,250 °C. After sintering at 1,400 °C for 4 h, the pure phase LSGM was obtained and the LSGM pellets get a relative density of 98%. Compared with the commercial TOSOH YSZ powder, the as-prepared LSGM powder has a fine particle size of 0.12 μm and narrow particle size distribution. The oxygen-ionic conductivity of the prepared samples reaches 0.08 S cm⁻¹ at 800 °C. To sum up, LSGM powders prepared by conventional solid-state reaction possess high purity, fine particle size, and high ionic conductivity. Dense and crack-free LSGM films supported by porous anode can be fabricated successfully using the prepared LSGM powders as starting materials.

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